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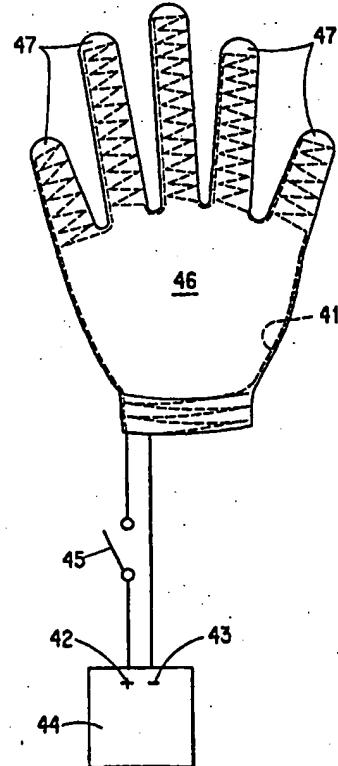
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(54) Title: HEATING FABRIC AND ARTICLES MADE THEREFROM

(57) Abstract

Heating fabric comprising textile fiber plated with conductive metal and articles made therefrom.



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HEATING FABRIC AND ARTICLES
MADE THEREFROM

5

Background of the Invention

A wide variety of heating devices has previously been developed using technology based on electrically conductive heating wires incorporated into a fabric. The heating wires generally have a conductive core with an electrical insulating layer surrounding the core. Current is passed through the conductive core which, by its resistance, causes the structure to heat.

Representative of previous electrically heated garments are those shown in Johnson U.S. Patent 3,644,705, which shows a low voltage, electrically heated shirt; Carrona U.S. Patent 3,084,241, which shows another electrically heated garment; Marsh U.S. Patent 3,663,797, which shows a football jersey having electrically heated pockets for warming the hands; and Yuasa U.S. Patent 3,751,620, which shows an electric garment with heating elements on the inside surface. Still another garment including a detachable heating module is shown in Kuo et al. U.S. Patent 5,148,002.

Previous heating structures and garments based on insulated wires have typically been bulky and limited in their configuration. A continuing need according exists for a fabric which has not only the ability to generate heat but a flexibility and conformability, combined with a light weight, that permit a wider variety of applications, especially in articles of clothing, than have heretofore been available. Particularly desirable would be a heating fabric in which the heating elements cannot be seen or felt.

35

Summary of the Invention

The instant invention provides an improved heating fabric that can be used in a wide variety of applications, including garments, and, at the same time, permits

washability of the final article in addition to excellent heating performance.

Specifically, the instant invention provides a heating fabric of textile filaments having incorporated therein at least one conductive yarn comprising substantially non-conductive filaments having at least about 10 weight % metal plated thereon, the conductive yarn being integrated into the fabric in a continuous resistive circuit having at least two terminals, the terminals being connected to an electric power source having a voltage of less than about 30, the conductive yarn being incorporated into the fabric in a density sufficient to provide at least about 5 watts per square foot of fabric when the power source is applied.

15

Brief Description of the Drawings

Figures 1 and 2 are planar views of fabrics with incorporated conductive yarn as used in the present invention.

20 Figure 3 is a cross-sectional view of a laminar structure of the present invention.

Figure 4 is an illustration of a glove of the present invention.

25 Figure 5 is an illustration of a sock of the present invention.

Detailed Description of the Invention

A central element of the present invention is conductive yarn comprising substantially non-conductive substrate fiber having metal plated thereon in a quantity of at least about 10 wt %, and generally about from 10 to 30 wt %. Less than about 10 wt % of the metal typically does not provide adequate conductivity for satisfactory performance as a heating element, while quantities greater than 60 wt % are difficult to incorporate into the fiber. A wide variety of polymers can be used for the preparation of these fibers, including polyesters, polyamides, polyacrylics and polyaramids. Non-polymeric fibers, such as those prepared from glass and carbon, can also be used.

However, polymeric fibers are preferred because of their flexibility and lack of brittleness.

Of the polymeric fibers, polyaramids are preferred in the present invention for the non-conductive polymer onto which the metal is plated. By "aramid" is meant a polyamide wherein at least 85% of the amide (-CO-NH-) linkages are attached directly to two aromatic rings. Aramid fibers which can be used are described in Man-Made Fibers - Science and Technology, Volume 2, in the section titled Fiber-Forming Aromatic Polyamides, page 297, W. Black et al., Interscience Publishers, 1968. Aramid fibers are also disclosed in U.S. Patents 4,172,938; 3,869,429; 3,819,587; 3,673,143; 3,354,127; and 3,094,511.

Para-aramids are the primary polymers in fibers used in this invention and poly (p-phenylene terephthalamide) (PPD-T) is the preferred para-aramid. By PPD-T is meant the homopolymer resulting from mole-for-mole polymerization of p-phenylene diamine and terephthaloyl chloride and also copolymers resulting from incorporation of small amounts of other diamines with the p-phenylene diamine and of small amounts of other diacid chlorides with the terephthaloyl chloride. As a general rule, other diamines and other diacid chlorides can be used in amounts up to as much as about 10 mole percent of the p-phenylene diamine or the terephthaloyl chloride, or perhaps slightly higher, provided only that the other diamines and diacid chlorides have no reactive groups which interfere with the polymerization reaction. PPD-T also means copolymers resulting from incorporation of other aromatic diamines and other aromatic diacid chlorides such as, for example, 2,6-naphthaloyl chloride or chloro- or dichloroterephthaloyl chloride; provided only that the other aromatic diamines and aromatic diacid chlorides be present in amounts which permit preparation of anisotropic spin dopes. Preparation of PPD-T is described in United States Patents No. 3,869,429; 4,308,374; and 4,698,414. In a particularly preferred embodiment, the fiber being plated with the metal comprises about from 70 to 98 weight % aramid and about from 2 to 30 weight %

polyvinylpyrrolidone (PVP) distributed throughout the fiber structure. It is believed that the presence of the PVP assists in providing sites for adherence of metal in the electroless plating process of the fibers. The reason 5 for improvement for plating adhesion is not fully understood.

By PVP is meant the polymer which results from linear polymerization of monomer units of N-vinyl-2-pyrrolidone with or without the inclusion of small amounts of 10 comonomers which may be present in concentrations below those which do not interfere with interaction of the PVP with the PPD-T or with metal cations.

It has been determined that PVP of nearly any molecular weight can be used in practice of this 15 invention. PVP of molecular weights ranging from as little as about 5000 to as much as about 500,000 can be used, and all will result in the benefits of this invention to some extent. PVP with a molecular weight of about 10,000 to about 40,000 is preferred, and 10,000 to 20 24,000 is most preferred. PVP with a molecular weight below about 5,000 does not appear to make a strong complex with the para-aramid PVP combination and is extracted easily from the fiber. PVP with a molecular weight above about 100,000, causes an increase in metal demand for a 25 minimum conductivity level. The reason for that increased metal demand is not understood.

Although the benefits of the PVP will be present at any concentrations of PVP, those benefits are difficult to measure at concentrations of less than about 2 weight 30 percent. The upper limit represents the concentration at which some qualities of the resulting fiber begin to deteriorate due to the presence of excess PVP. It should be recognized that PVP is not known to be an outstanding or even impressive fiber forming material; and that, even 35 though its presence in fibers in combination with PPD-T yields fibers of excellent and entirely unexpected improvements, there is a concentration for the PVP above which some qualities of the fibers are not acceptable. It is believed that above about 30 weight percent of PVP,

based on PPD-T, the PVP is irreversibly leached from the fiber into the coagulation bath during manufacture.

Additives can be used with the aramid, and it has been found that up to about 10 percent, by weight, of 5 other polymeric material can be blended with the aramid or that copolymers can be used having up to about 10 percent of other diamine substituted for the diamine of the aramid or up to about 10 percent of other diacid chloride substituted for the diacid chloride or the aramid.

10 Fibers used in the present invention can be spun using the process of European Patent Publication No. 401,740, published December 12, 1990 wherein an agitated anisotropic mixture of acid solvent, para-aramid, and PVP is heated and extruded through a spinneret, into and 15 through a non-coagulating layer, and into and through an aqueous coagulating bath. Elements of that process, using PPD-T alone, are taught in United States Patent No. 3,767,756, issued October 23, 1973. Fibers can be used in this invention as-spun or heat treated.

20 In general the metalized fibers used in the present invention can be prepared by first contacting the surface of a fiber structure with an aqueous solution of activating cations of the metal to be applied, thereby adhering the activating metal cations to the surface of 25 the polymer structure; rinsing the surface of the structure to remove nonadherent activating metal cations; immersing the rinsed surface in an aqueous solution of metal cations to be plated and a reducing agent. The quantity of metal plated onto the fiber will necessarily 30 vary with the intended use as well as the conductivity or resistivity of the metal used. In general, however, the metal will comprise about from 10 to 60 wt % of fiber, and will be plated to provide a resistance of about from 10 to 20 ohms in the complete circuit in a typical fabric. In 35 general, fibers having about from 20 to 50 wt % plated metal have been found to be particularly satisfactory, and are accordingly preferred. The preferred level of resistance is important to the application of low voltage power.

The metal to be plated on the fibers can be selected from any autocatalytically platable metal which imparts the desired conductivity. Preferred metals include silver, copper, nickel and gold, of which silver is 5 particularly preferred.

Prior to the plating operation, the fibers to be plated can be treated to promote adhesion. For example, depending on the particular fiber used in the plating operation, a wash with an acid bath will improve adhesion 10 of the metal plated onto the fiber by disrupting the surface of the fiber being plated.

Fibers of para-aramid/PVP can be plated by the following general process.

An aqueous activation bath is prepared using 15 appropriate activating cations, among which stannous is preferred. Para-aramid fibers to be plated are immersed in the bath and agitated to promote the activation. The fibers are removed from the activation bath and rinsed until there is substantially no activating cation in the 20 rinse water.

The rinsed and activated fibers are placed in another aqueous bath which will become the plating bath and which can optionally include a surfactant to assist in complete wetting. The surfactant is preferred but not necessary 25 and, if used, should be nonionic and should be used at a concentration of about from 1 to 5 grams per liter of bath.

A metal complex solution is added to the fibers to form the plating bath. The metal complex solution is made 30 by dissolving the appropriate amount of metal salt, such as silver nitrate, in water followed by addition of ammonia until the solution is a light straw color and has pH of about 8-9.5, and preferably about 9. The appropriate amount of metal salt is that amount which will 35 provide the desired weight of reduced metal as a function of the fiber material to be plated. For example, if it is desired to make a "40 percent bath", there must be enough silver nitrate to provide reduced silver in a weight of 40% of the weight of the fiber to be plated in the bath.

Baths having a wide range of metal concentrations can be used in practice of this invention. The preferred plating baths are about from 30 to 45 percent silver. It has been found that baths of 35 to 40 percent silver are 5 most effective and most preferred.

The total volume of the plating bath should be such that the concentration of the silver nitrate is less than about 10 grams per liter. It has been found that metal complex solutions which are too concentrated in the metal 10 cations may yield free metal granules rather than a strongly adherent metal coating.

The plating bath, with immersed fibers, is moderately agitated for 10 to 20 minutes to assure near equilibrium of the system; and then formaldehyde is added to the bath 15 as a reducing agent. The formaldehyde is generally added as a 37, weight percent, aqueous solution; and is added in an amount to constitute a mole ration with the silver of 1.1/1 to 2/1, or more. The formaldehyde can be added all at once or in increments over a period of time. For 20 example, it has been found to be useful to add the formaldehyde in 10% increments over the course of an hour, or so. The agitation is preferably continued until an analysis of the plating bath reveals silver residuum of less than about 5 parts per million. The plated material 25 can then be rinsed and dried.

All of the above steps can be conducted with the various baths at temperatures of about from 10 to 60°C, and preferably about 20-40°C.

The plated fiber can be incorporated into a fabric by 30 any convenient means, including, for example, weaving or knitting the conductive fiber into the fabric or placing the conductive fiber in the desired circuit pattern between two layers of fabric to anchor the filament into position. In a further alternative embodiment of the 35 present invention, a woven fabric can be plated with the desired metal, and the plated fabric then cut into strips for incorporation into a garment. Similarly, the plating techniques can be applied to paper or spun bonded fabrics, which can be similarly cut into strips for incorporation

into a garment by either weaving into the garment or laminating the conductive fabric strips between two layers of the basic garment fabric. In the preparation of a fabric, the metal plated fibers can be reexpanded by 5 combing, to separate the individual filaments and expand a single bundle of fibers into a planar configuration. This provides a more uniform heating surface, while not disrupting the electric connection of the circuit provided by the conductive fiber.

10 The circuitry of the conductive fiber provided in the heating fabric should be sufficient to provide a heating capacity of at least about 5 watts per square foot. The density of the conductive fiber in the fabric will necessarily vary with many factors, including the size of 15 the fiber, the weight of the metal plating, and the density of the weave or knit of the fabric. However, by way of illustration, for a textile fiber of 1500 denier having 40 wt % silver plated thereon, effective heating in a fabric can be achieved with one plated fiber present 20 per inch of fabric in a longitudinal array.

The electrical source for the conductive elements of the present fabric can be based on either alternating current or direct current. In general, for portability, direct current is preferred, particularly for garments. 25 The source used can be of the type conventionally used in portable power tools and the like, typically generating a voltage of about from 5 to 15 volts, which is preferred for garment applications. Batteries comprising a pack of rechargeable battery cells, for example, each of a nominal 30 1.2 vdc, can be used. Thus, a battery pack with six rechargeable cells will provide a power supply of 7.2 vdc. Nickel-metal hydride cells have been found to be particularly satisfactory.

Multiple batteries can be used in the present 35 invention to provide the voltage necessary for the desired level of heating within the fabric or garment. Using multiple batteries, alternative wiring of these batteries provide for an initial series connection for increased voltage in the system can provide an increased power level

for initial warm-up period; after which the usual parallel configuration for the multiple batteries can be resumed. In heating pads or heating blankets, a standard 120 volt power supply can be converted to low voltage DC current by 5 rectifying circuitry, thus eliminating the proximity of high voltage current next to the user. In addition, systems in which alternating current is converted to lower voltage direct current can provide for initial higher start-up currents that bring the heating fabric quickly to 10 its desired operating temperature, after which low voltage levels can be maintained for steady state operation.

The voltage applied to the fabric, to permit contact with a wearer without discomfort or negative consequences from the electrical current being passed through the 15 fiber, should be less than about 30 volts, and preferably less than about 20 volts, although voltages of up to about 35 can generally be used without any adverse effect.

The present invention is further illustrated in the figures, in which Figures 1 and 2 are planar views of 20 fabrics incorporating the metalized fiber used in the present invention. In Figure 1, the metalized fiber 1 is embedded in fabric 2 in a continuous series circuit terminating in ends 3 and 4. The ends are attached to electrical source 5, operated by switch 6.

25 A similar configuration is shown in Figure 2, except that the metalized fiber is arranged to provide a parallel circuit. In general, a series circuit pattern, as shown in Figure 1, is preferred.

Figure 3 illustrates a representative laminar 30 structure that can be used, for example, for blanket or heating pad applications. There, a fabric of the present invention, generally identified as 30, and having conductive yarn 31, is combined with insulating material 32 and outer protective layer 33. In this manner, the 35 heating layer can be placed adjacent to the surface to be heated, the insulating layer maximizing the efficiency of the heating element.

A further embodiment of the present invention is shown in Figure 4, which is an illustration of a glove

according to the present invention. There, plated wire 41 with terminal ends 42 and 43 attached to battery 44 and switch means 45. The conductive fibers are arranged within the glove means 46 having finger portions 47 to 5 concentrate the density of the pattern in the finger portions, thus providing the greatest heat at that part of the construction.

A similar construction is shown as a sock in Figure 5, in which the metal plated fiber is incorporated 10 primarily in the toe portion 51.

The articles of the present invention provide marked advantages over heating devices previously known. The use of a metalized fiber as opposed to an insulated solid metal conductor permits the preparation of a finished 15 article that has a light weight, softness and flexibility normally characteristic of fabrics without the solid metal conductors incorporated into the fabric. The fine fibers used in the present invention permit placement of the fibers and, accordingly, provision of heat, with much 20 greater precision than would be possible using stiffer insulated metal conductors. Accordingly, as illustrated particularly in Figure 4 and 5, the metal plated fibers used in the present invention can be used to form intricate patterns within a garment, specifically 25 concentrating the heating capability of the plated fiber where it is needed most, thereby making the most efficient use of the limited battery power available for a system. Moreover, the flexibility and durability of the metal-coated or plated fibers permit washing without substantial 30 disruption of the electrical conductivity of the metal coated fibers incorporated in the fabric. In addition, the plated fiber can itself be knitted and woven into a fabric, optionally in conjunction with elastomeric filaments so that the fabric is stretchable in at least 35 one direction.

This combination of properties makes the present fabric ideally suited for outdoor garments for various sporting applications, including both spectators and participants. The fabric can be incorporated into boots

and gloves for hunters or fishermen and can be adapted as a lap blanket in open carriages. Similarly, the fabrics may be fabricated into a wide variety of clothing for construction and repair personnel. Each of these 5 applications is particularly desirable since the heating elements in the construction can be incorporated so that they are neither seen nor felt.

A wide variety of medical needs can be met by the present fabrics, including hypothermia blankets, heating 10 pads and flexible bandages for sports injuries. In addition, the combination of heat and electrical energy can be used to advantage for bone healing applications in which a low level of electrical current facilitates tissue growth.

15 The invention is further illustrated by the following specific example.

EXAMPLE

A continuous filament yarn of 85% poly (p-phenylene 20 terephthalamide) (PPD-T) and 15% PVP (40,000 MW), having 1000 denier and about 665 filaments, was soaked for 20 minutes in a solution of 45.6 grams of stannous chloride in 400 ml of water having the pH adjusted to about 1.5 with HCl. The yarn was then rinsed with water and placed 25 in silver nitrate solution to plate silver onto the yarn. The solution contained 415 grams of silver nitrate, 3 ml of nitric acid solution, and 315 ml of 37% formaldehyde, all in 400 ml of water, to which ammonium hydroxide was added to reach a pH of about 9. In this solution, silver 30 spontaneously plated onto the yarn, to provide a plated yarn having about 33% by weight of plated silver.

The yarn was incorporated into a knit fabric in series circuit pattern, resulting in a spacing between the conductive fibers in the fabric of about 1 cm. A battery 35 pack was attached to the terminal ends of the conductive fiber to provide a power input of 12 volts. The fabric, having surface area of several square feet, was elevated in temperature to about 70°C.

I CLAIM:

1. A textile fabric having incorporated therein at least one conductive yarn comprising substantially non-conductive filaments having at least about 10 wt % metal plated thereon, the conductive yarn being integrated into the fabric in a continuous resistive circuit having at least two terminals, the terminals being connected to an electric power source having a voltage of less than about 30, the conductive yarn being incorporated into the fabric in a density sufficient to provide at least about 5 watts of power per square foot of fabric when the power source is applied.
5
2. A fabric of Claim 1 wherein the substantially non-conductive filaments consist essentially of synthetic polymer.
15
3. A fabric of Claim 2 wherein the synthetic polymer consists essentially of polyaramid.
4. A fabric of Claim 3 wherein the aramid further comprises about from 2 to 30 weight % polyvinylpyrrolidone (PVP).
20
5. A fabric of Claim 1 wherein the metal of the conductive fiber is selected from the group consisting of silver, copper and nickel.
6. A fabric of Claim 1 wherein the metal consists essentially of silver.
25
7. A fabric of Claim 2 wherein the conductive yarn has a denier of at least about 500.
8. A fabric of Claim 7 wherein the conductive yarn has a denier of at least about 1000.
30
9. A fabric of Claim 1 wherein the metal is present in an amount sufficient to provide a resistance of about from 10 to 20 ohms.
10. A fabric of Claim 1 wherein the power source generates direct current.
35
11. A fabric of Claim 1 in the shape of garment.
12. A garment of Claim 11 in the configuration of a glove.

13. A garment of Claim 12 wherein the conductive filaments are concentrated in the finger portions of the glove.

14. A garment of Claim 11 in the configuration of a
5 sock.

15. A garment of Claim 14 wherein the conductive fibers are most heavily concentrated in the toe portions of the sock.

16. A fabric of Claim 1 in the configuration of a
10 blanket.

17. A fabric of Claim 1 in the configuration of a heating pad.

18. A fabric of Claim 17 further comprising an insulating layer adjacent the fabric.

15 19. A fabric of Claim 1 which is stretchable in at least one direction.

FIG.1

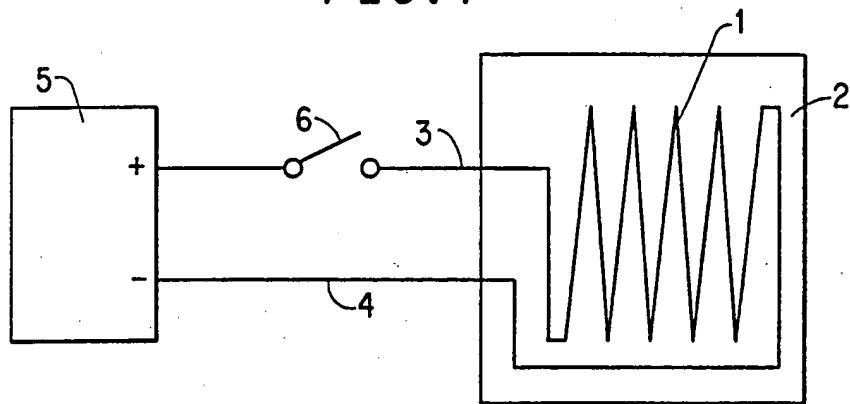


FIG.2

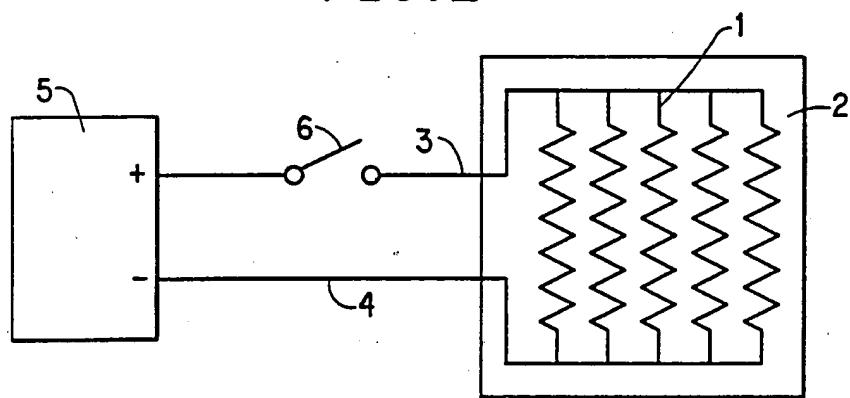


FIG.3

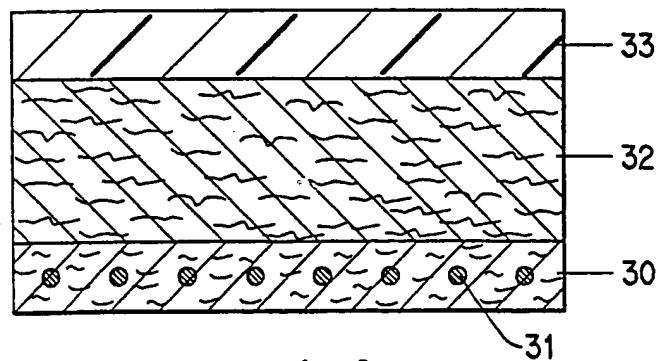


FIG.4

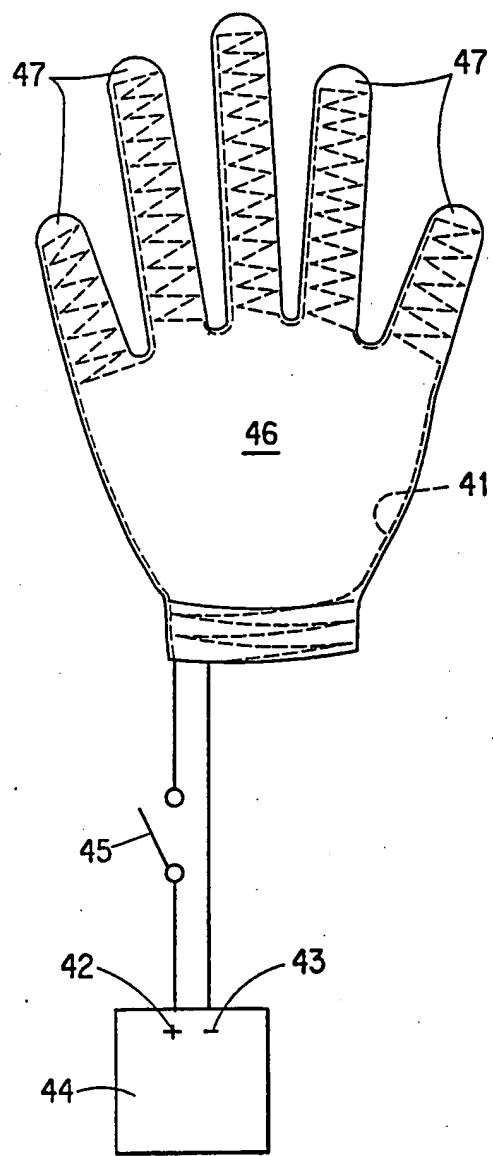
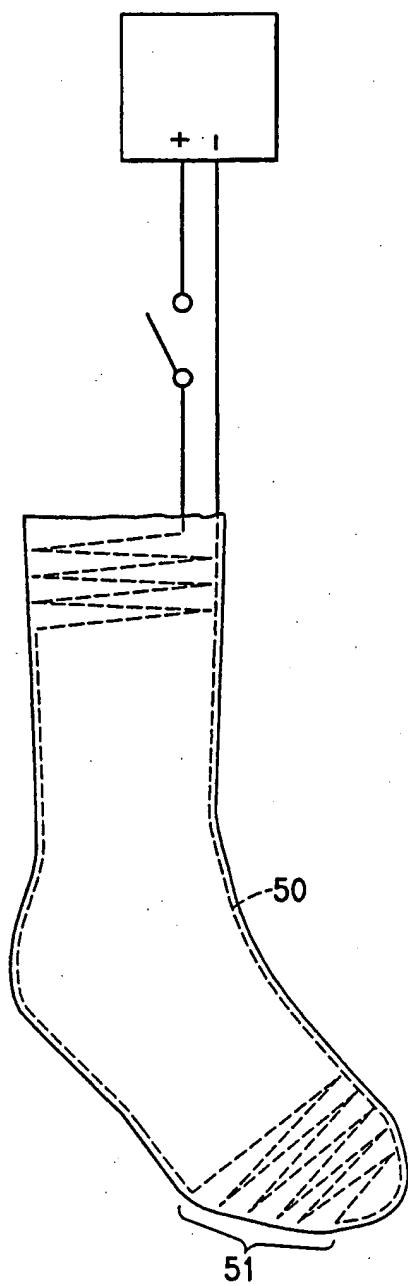


FIG.5



INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US 95/05860A. CLASSIFICATION OF SUBJECT MATTER
H 05 B 3/36

According to International Patent Classification (IPC) or to both national classification and IPC6

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H 05 B, H 05 B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE, A, 2 537 342 (IMPERIAL CHEMICAL INDUSTRIES) 04 March 1976 (04.03.76), page 1, last paragraph - page 2, line 8; page 7, third paragraph; claims 1,4-6. --	1,2, 10-12, 14,16, 17
D,Y	US, A, 3 751 620 (YUASA) 07 August 1973 (07.08.73), column 2, lines 15-22,46-52; claims; fig. 1-4. --	1,2, 10-12, 14,16, 17
A	GB, A, 635 230 (E. DAMOND) 05 April 1950 (05.04.50), page 1, lines 8-15; page 2,	1, 16-18

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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Date of the actual completion of the international search
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INTERNATIONAL SEARCH REPORT

-2-

International Application No
PCT/US 95/05860

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>lines 2-6, 17-29; claim 1; fig. 5, 7-10. --</p> <p>US, A, 2 631 219 (C.T. SUCHY) 10 March 1953 (10.03.53), column 1, lines 13-19; column 4, lines 9-43; claim 1; fig. 1-4. -----</p>	1, 2, 16-18

ANHANG

zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

ANNEX

to the International Search Report to the International Patent Application No.

ANNEXE

au rapport de recherche international relatif à la demande de brevet international n°

PCT/US 95/05860 SAE 110177

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unter-richtung und erfolgen ohne Gewähr.

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Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
DE A1 2537342	04-03-76	AU A1 84163/75 GB A 1525851	24-02-77 20-09-78
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US A 2631219		keine - none - rien	